# Effect of high pressure on the thermoelectrical properties of single-walled and double-walled carbon nanotubes

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# Effect of high pressure on the thermoelectrical properties of single-walled and double-walled carbon nanotubes

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**Abstract.** The effect of high pressure on the Seebeck coefficient and temperature dependences of the electrical resistance of single-wall and double-walled carbon nanotubes was studied in order to detect phase transformations occurring in carbon nanotubes in the pressure range 4–46 GPa. Diamond anvil cells with conductive synthetic diamonds were used to create high pressures. We observed a number of features associated with the structure changes of nanotubes. Temperature dependences of the electrical resistance of single and double-walled carbon nanotubes have the form characteristic of nondegenerate semiconductors. Analysis of results indicates the destruction of the structure of carbon nanotubes at high pressure.

## 1. Introduction

Carbon nanotubes are the subjects of numerous experimental and theoretical studies since its discovery by Iijima in 1991 [1]. Such attention of researchers is connected with great prospects of possible applications of carbon nanotubes in different fields of science and technology. The unique mechanical, thermal and electrical properties of carbon nanotubes (CNTs) depend on the number of layers (walls), diameter and chirality. Due to abnormally high mechanical properties, carbon nanotubes are the one of the most efficient materials suitable for creating of high-strength composites [2]. There are many examples of creating various nanoscale devices based on carbon nanotubes [3, 4]. These structures attract such attention of researchers, first of all, because of the possibility of regulating the conductivity of the nanotube by changing it structure [5].

Studies of CNTs under pressure revealed the features of their mechanical characteristics [6–9]. It was shown by methods of molecular dynamic modeling [10–13] and experimentally [8, 14] that single-walled carbon nanotubes (SWCNTs) under pressure undergo structural phase transitions corresponding to the distortion of the cross-sectional shape of the nanotube from round to oval and flattened. The $P_c$ pressure at which the SWCNT collapses is inversely proportional to the cube of the nanotube diameter [8]. Deformation of nanotubes of small diameter (less than 1 nm) occurs continuously.

In the case when the diameter of nanotubes exceeds 1 nm, pressure hysteresis and first order phase transitions are observed [9]. A similar structural transition was observed at $P_c$ pressure of about 1–1.5 GPa in multi-walled carbon nanotubes (MWCNTs) [15] and polymer composites

based on MWCNTs [16]. At pressure more than 30 GPa irreversible changes occur with the formation of new structures based on nanotubes [8, 9]. In addition, a compressive force of 45–65 GPa combined with shear deformation at room temperature leads to the bonding of carbon nanotubes and the formation of graphite fragments connected by $sp^3$-bonds. In particular, SWCNTs [6, 17] or MWCNTs [18, 19] turn into onions with layers connected by $sp^3$-bonds. Many structures formed by carbon nanotubes are stable after load reduction [9, 17–19].

Double-walled carbon nanotubes (DWCNTs) consist of two concentric carbon monolayers, which can have different structural and electrical characteristics. In DWCNTs, the outer tube protects the inner one from chemical and mechanical impact, while the inner tube is the mechanical support for the outer one. It was previously shown that DWCNTs are more resistant to mechanical stress than single-walled nanotubes or SWCNTs filled with fullerenes [20]. Double-walled carbon nanotubes also exhibit a series of structural transitions similar to those observed in single-walled nanotubes [7,14]. The results of recent studies have revealed a two-stage mechanism of destruction of double-walled nanotubes [20], which is explained by the sequential destruction of the outer and then the inner nanotube.

Previously we carried out investigations of high pressure effect on the electrical resistance and structure of double-walled CNTs using Raman scattering technique [21].

The aim of this study is to study the effect of high pressure on the thermoelectric properties of single-walled and double-walled carbon nanotubes. Structural transformations of carbon nanotubes under high pressure must be accompanied by the variation of their electrical and thermal properties. Therefore, obtained results provide additional information on structural transformations in carbon nanotubes under high pressure.

## 2. Experiment

In this study, we used bundles of single-walled nanotubes with a diameters from 0.8 to 1.8 nm, and bundles of double-walled nanotubes with an external diameters 4±1 nm and a length of 1–5 $\mu$m. The nanotubes were synthesized using the chemical vapor deposition (CVD) technique.

Pressure up to 50 GPa was created in a cell with electroconductive diamond anvils (DACs) of the "round cone-plane" type from synthetic carbonado diamonds. These synthetic diamonds are good conductors and thus allow us to study the electrical properties of samples at high-pressure [22]. The resistance of short-circuited anvils is 7–12 Ohms and varies slightly with temperature. Samples compressed in the DAC had diameter about 200 $\mu$m and were about 20 $\mu$m thick. The DAC calibration data and technical details are given in [23]. The error of the pressure measurements did not exceed 10% in the pressure range from 20 to 50 GPa.

The resistance of the samples was measured at temperatures of 77–400 K. The temperature of the DAC was recorded using a copper–constantan thermocouple. The relative systematic error of electrical resistance measurement did not exceed 1%. The technique allows to study the sample at sequential pressure increasing and decreasing, to withstand it under load for a long time [23, 24]. The pressure was created at room temperature, after which the cell was cooled to the temperature of liquid nitrogen. Temperature dependences of electrical resistance were measured at slow heating of DAC [24].

The upper anvil was heated in the process of measuring the Seebeck coefficient to obtain a temperature gradient. The temperature of the anvils at the contact points was measured by two copper–constantane thermocouples. The absolute value of the coefficient $S$ was calculated by measuring the induced potential difference through the copper branches of thermocouples:

$$S = S_{\mathrm{Cu}} + \frac{U_{12}}{T_1 - T_2}, \tag{1}$$

where $S_{\mathrm{Cu}}$ is the absolute thermal emf of copper (1.8 $\mu$V K$^{-1}$), $U_{12}$ is the measured thermal emf, and $T_1$ and $T_2$ are temperatures of the heated and the cool ends of the sample [25]. At

measuremets of the Seebeck coefficient the temperature difference between the cold and hot faces of the sample was about 1 K. Accuracy of the temperature measurement was about 0.05 K [26].

Measurements of the Seebeck coefficient were carried out with a gradual pressure increasing from 4 to 46 GPa. For samples with a low value of thermal EMF (e.g., copper) the relative error of the Seebeck coefficient did not exceed 10%. The sample was kept for a certain time at each pressure loading before the measurement. Then the pressure gradually decreased from 46 GPa to the initial value 4 GPa [25].

## 3. Results and discussion

In the configuration, we use the sign of the Seebeck coefficient, and its value corresponds to the electronic type of charge carriers, which is typical for a semiconductor material.

Figure 1 shows the results of two successive measurements of the pressure dependences of the Seebeck coefficient of a single-walled CNT sample. The value of the Seebeck coefficient decreases with increasing pressure throughout the studied range in each of the two measurement cycles. In the first cycle, when the pressure increases, there is a small increase in the coefficient $S$ in the range of 18–24 GPa [figure 1($a$)]. A similar feature is observed in the second cycle at 24–26 GPa [figure 1($b$)]. When the pressure decreases this feature is observed only in the first cycle of measurements.

The inflection points on the dependence of the coefficient $S$ upon pressure can probably be explained by structural transformations associated with the collapse of nanotubes of various diameters. The nature of the pressure dependences of the Seebeck coefficient indicates the partial reversibility of the transformations occurring in the sample.

The pressure dependence of the coefficient $S$ of double-walled carbon nanotubes has a similar character. However, in each of the three measurement cycles, the dependencies have certain features associated with structure changes of the nanotubes. The sign of the coefficient $S$ and its value, taking into account the device of the experimental installation and the connection scheme, as well as in the case of single-wall nanotubes, indicates the electronic type of charge carriers. The character of the baric dependences of the Seebeck coefficient of double-walled carbon nanotubes demonstrates the partial reversibility of the phase transformations occurring in the sample under pressure.

In the first cycle, when the pressure increases, there are two inflection points at pressures 16 and 26 GPa. When the load decreases, only one such feature is observed at 18 GPa [figure 1($c$)]. In the second cycle, two inflection points are visible on both curves: about 18 and 26 GPa in case of pressure increasing, 20 and 28 GPa in case of pressure decreasing [figure 1($d$)].

At the next retrying of the experiment [figure 1($e$)] observed the same features as in the second experiment, but in this case they are more pronounced. Also in the third cycle the pressure hysteresis in the range less than 28 GPa is more distinct.

These features of the Seebeck coefficient are associated with the collapse of nanotubes with different diameters. At a pressure of about 25 GPa, the destruction of external nanotubes in double-walled CNTs of the largest diameters occurs, which was previously shown in [21]. The observed features of coefficient $S$ in the second and third measurement cycles are associated with reversible collapse of smaller diameter nanotubes [figure 1($d$,$e$)]. Growth of hysteresis width of Seebeck coefficient [figure 1($e$)] is caused by the processes of destruction of the structure of double-walled CNTs and an increase in the number of $sp^3$-hybridized atoms [21].

Figure 2 shows the temperature dependence of the electrical resistance of single-walled carbon nanotubes at pressures from 20 to 44 GPa. The dependences $R(T)$ have the form characteristic of nondegenerate semiconductors. Temperature dependences of resistance demonstrate the activation character with two activation energies. The change of slope as a function of $R(T)$ is observed at different temperatures as a function of pressure. Thus, at $P = 20$ GPa the change of curve slope occurs at a temperature of 297 K; in the pressure range 22–30 GPa—at a temperature

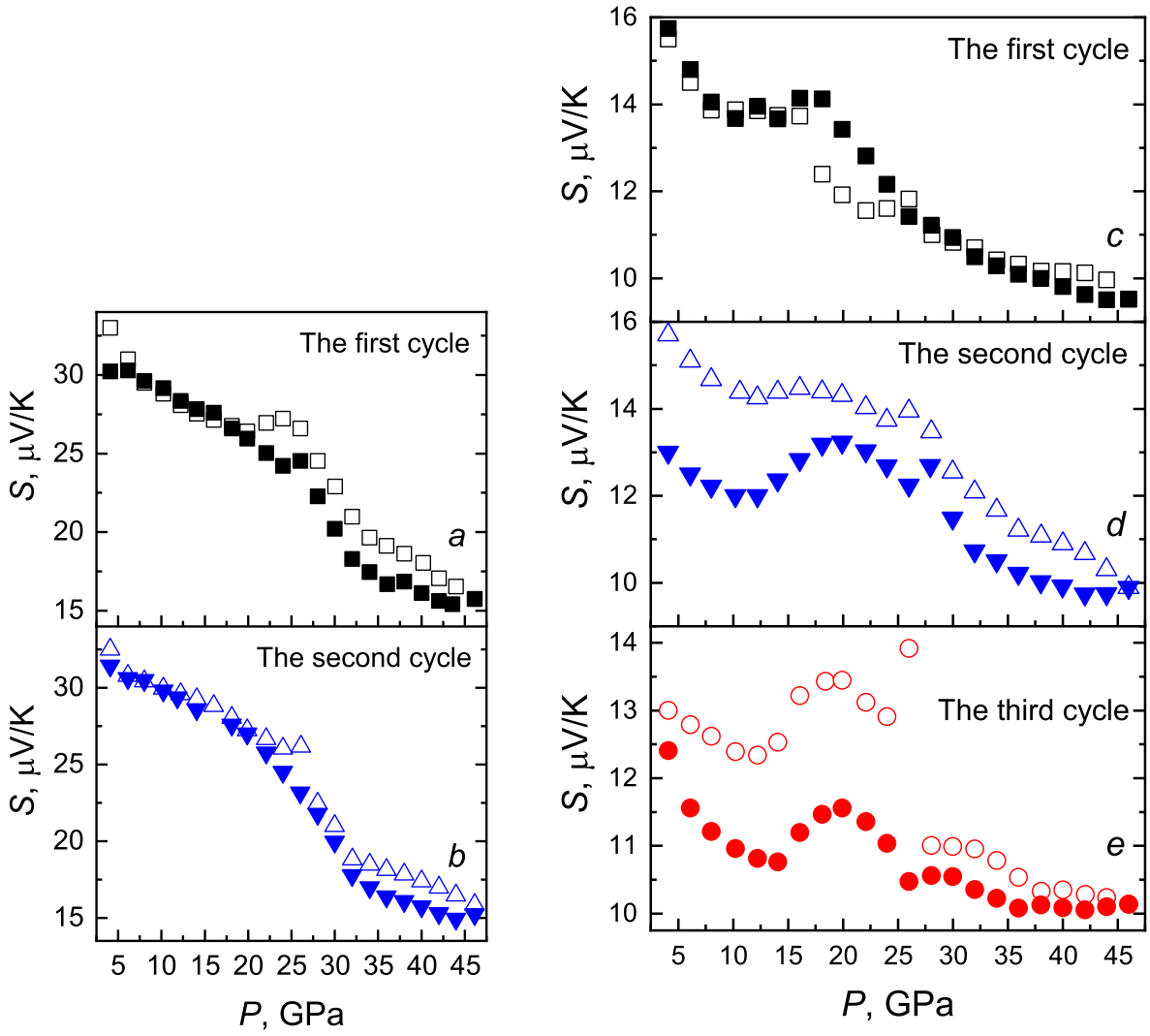


**Figure 1.** The baric dependences of Seebeck coefficient of the SWCNTs and DWCNTs samples: $(a, b)$ SWCNTs first and second measurement cycles; $(c, d, e)$ DWCNTs first, second and third measurement cycles; open and solid symbols signify the data obtained during compression and decompression, respectively.

about 125 K; at pressure 44 GPa—at temperature of about 150 K. Also the features in the form of inflection points are observed at pressure 20 GPa about 227 K; in the range of 22–30 GPa at a temperature about 225 K, and at 44 GPa at 260 K. The dependence of electrical resistance on temperature decreases significantly with increasing pressure and increases with decreasing pressure. This is clearly observed at pressures greater than 30 GPa.

Figure 3 shows the temperature dependence of the electrical resistance of DWCNT bundles obtained at pressure from 20 to 46 GPa. At temperatures up to 210–225 K (for different pressures) dependences $R(T)$ have the form characteristic of nondegenerate semiconductors. However, with a further temperature increasing dependence of $R(T)$ becomes more complicated. For example, at 20 GPa there are two inflection points: about 250 and 350 K. With a further pressure increasing there is only one such feature at temperature of about 250 K. In addition, in each of the dependencies at 380 K the resistance begins to increase and when the pressure is

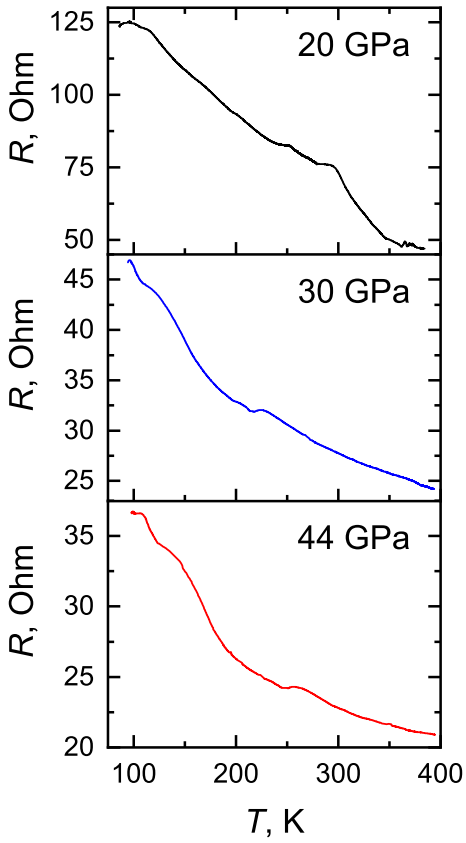


**Figure 2.** The temperature dependences of the electrical resistance of SWCNTs in the pressure range of 20–44 GPa.

higher, that the faster the resistance increases. At pressures of 35–40 GPa and at temperatures more than 280 K the temperature dependences take the metal-like form. However, at 46 GPa dependence $R(T)$ is similar to those observed at pressures below 35 GPa. Probably, these conditions stimulate to the formation of $sp^3$-bonds, which causes the transition of a certain number of nanotubes to the graphite-like phase.

It should also be noted, that dependence of electrical resistance on temperature decreases significantly with a pressure increasing. It is especially obvious at pressures greater than 30 GPa. This effect is observed in both samples and is in good agreement with our results of electrical measurements obtained earlier for the same carbon nanotubes [21].

Such character of temperature dependences of electrical resistance and baric dependences of the Seebeck coefficient can be explained by formation of two-dimensional or three-dimensional structures on the base of nanotubes [9]. At some critical pressure bonds are formed between two flattened regions of the nanotube or neighboring nanotubes. Such transformations lead to an increase in the proportion of disordered that is $sp^3$-hybridized atoms in the sample under study and must be accompanied by a change in electrophysical properties. However, it is more likely that the formation of such structures stable after decompression requires additional use of shear strains [17–19].

It is most probably that the observed pattern is due to the processes of destruction of the structure of CNTs. Transformations of the structure of SWCNTs occurring at pressure about 44 GPa can be partially reversible. It is also confirmed by temperature dependences of electrical

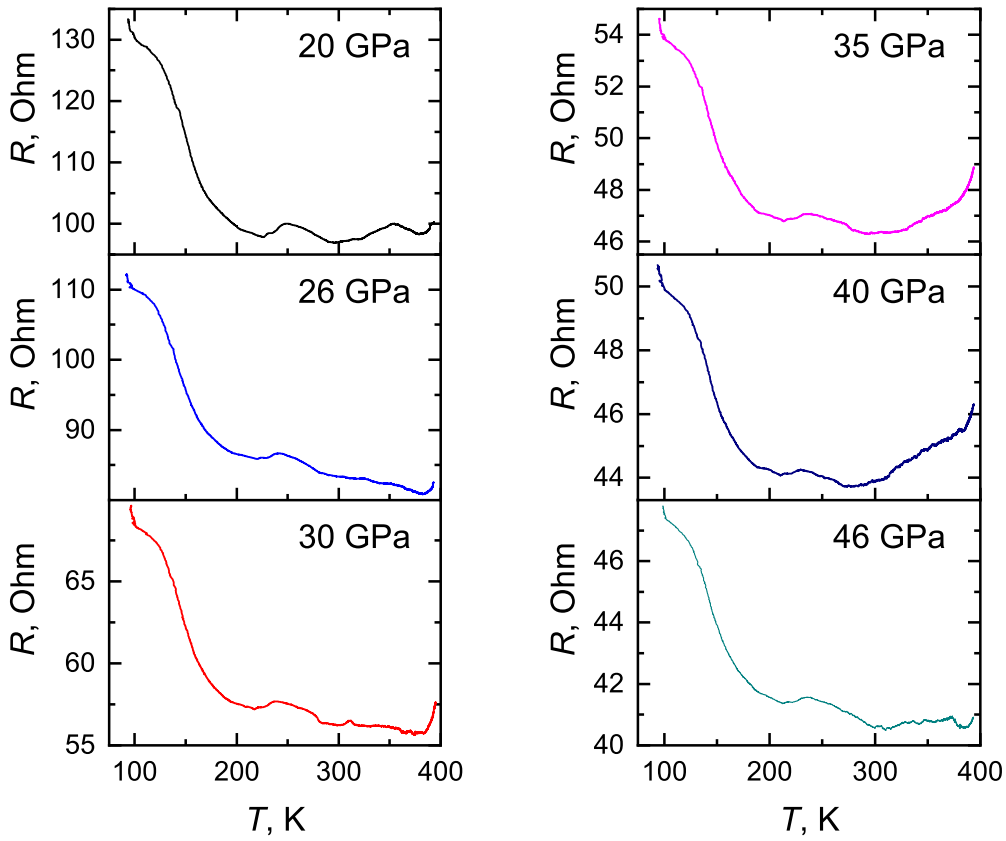


**Figure 3.** The temperature dependences of the electrical resistance of DWCNTs in the pressure range of 20–46 GPa.

resistance. In the case of DWCNTs, there is a collapse of nanotubes of different diameters and the destruction of external nanotubes of the largest diameters. In addition, the results presented in this paper are in good agreement with previous studies of the effect of high pressure on the electrical properties and structure of double-walled carbon nanotubes, performed earlier for the same samples [21]. In particular, the electrical resistivity features associated with changes in the structural state of the sample of two-layer nanotubes are observed at the same pressures as similar features in the dependences of the Seebeck coefficient.

## 4. Conclusion

We found a strong effect of pressure upon the thermoelectric characteristics of single-wall and double-wall carbon nanotubes that can be attributed the structural transformations in nanotubes under high pressure. The features of the Seebeck coefficient in the pressure range 16–42 GPa are associated with the collapse of nanotubes and the processes of destruction of the structure of nanotubes of different diameters. The temperature dependences of the electrical resistance $R(T)$ of the investigated carbon nanotubes have the form similar to those of nondegenerate semiconductors.

Obtained results evidence the processes of destruction of the structure of carbon nanotubes under pressure. Therefore, the study effect high pressure on the thermoelectric characteristics can be used as additional tool to revealing of structural transformations in carbon nanotubes.

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